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(54) **PROCESS FOR REPROCESSING A SPENT NUCLEAR FUEL AND OF PREPARING A MIXED URANIUM-PLUTONIUM OXIDE**

VERFAHREN ZUR WIEDERAUFBEREITUNG VON VERBRAUCHTEM KERNBRENNSTOFF UND
ZUR HERSTELLUNG EINES GEMISCHTEN URAN-PLUTONIUM-OXIDS

PROCÉDÉ DE RETRAITEMENT D'UN COMBUSTIBLE NUCLÉAIRE ÉPUISÉ ET DE PRÉPARATION
D'UN OXYDE MÉLANGÉ D'URANIUM-PLUTONIUM

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Description

TECHNICAL FIELD

[0001] The present invention relates to a novel process for reprocessing a spent nuclear fuel, based on uranium oxide or on mixed uranium-plutonium oxide, which makes it possible for the uranium and plutonium to be very effectively decontaminated from other chemical elements contained in this fuel without leaving, at any moment during this process, plutonium without uranium, so as to minimize the risk of misappropriating the plutonium for military purposes.

[0002] The process of the invention also makes it possible to obtain, at the end of this decontamination, a mixed uranium-plutonium oxide powder that can be used directly in processes for manufacturing MOX (**M**ixed **O**Xide Fuel) nuclear fuels, such as the MIMAS (**M**icronized **M**ASter Blend) process.

PRIOR ART

[0003] At the present time, all plants for reprocessing spent nuclear fuels use the PUREX (**P**lутonium **U**ranium **R**efining by **E**Xtraction) process for recovering the uranium and plutonium that are present in these fuels.

[0004] This is obtained by carrying out several purification cycles using the liquid-liquid extraction technique (that is to say by mixing an aqueous phase and a solvent phase that are mutually immiscible, followed by separation of these two phases by settling) which is carried out in multistaged units of the mixer/settler type, pulsed columns or centrifuge extractors, which are connected in series so as to allow these cycles and the various operations that they comprise to be carried out continuously.

[0005] The PUREX process, as implemented in modern reprocessing plants such as UP3 and UP2-800 plants on the Areva NC site at La Hague in France, or Rokkasho plant in Japan, schematically comprises three purification cycles: a first cycle, the purpose of which is essentially to decontaminate both the uranium and the plutonium from the fission products and from two minor actinides, namely americium and curium, and also to partition these two elements into two separate streams; and two complementary cycles called the "*second plutonium cycle*" and "*second uranium cycle*", respectively, the purpose of which is to purify the plutonium and the uranium after their partition.

[0006] The first cycle starts with an operation which consists in extracting both the uranium and the plutonium, the first being in oxidation state (VI), and the second being in oxidation state (IV), from the aqueous phase in which they are found.

[0007] This aqueous phase is obtained by dissolving a spent fuel in nitric acid and clarifying the mixture thus obtained. This phase is commonly called the "dissolution liquor".

[0008] The coextraction of the uranium and plutonium

is carried out by means of a water-immiscible solvent phase that contains an extractant having a high affinity for uranium(VI) and for plutonium(IV), in this case tri-n-butyl phosphate (or TBP) used with a concentration of 30% (v/v) in an organic diluent, in this case a dodecane. The uranium and the plutonium thus pass into the solvent phase, while most of the fission products, americium and curium remain in the aqueous phase.

[0009] It is followed by one or more scrubbing operations in which the solvent phase is scrubbed by one or more aqueous nitric phases of different acidities, so as to remove the fission products from said solvent phase that were extracted with the uranium and the plutonium.

[0010] The aqueous phase or phases resulting from these coextraction and scrubbing operations (or raffinate), which are laden with fission products, are removed from the cycle whereas the solvent phase, which is itself laden with uranium(VI) and with plutonium(IV), is directed to a zone in which the partition of these two elements is carried out.

[0011] This partition comprises:

- an operation for the purpose of back-extracting the plutonium from the solvent phase by means of an aqueous nitric phase of low acidity, containing a reducing agent capable of reducing plutonium(IV), which is highly extractable by TBP, to plutonium(III) which is itself only barely extractable, and to do so without reducing the uranium, and also a nitrous acid scavenger, the role of which is to stabilize both the uranous nitrate and the plutonium(III) by destroying the nitrous acid that tends to form in the aqueous nitric phase; in this case the reducing agent is uranous nitrate, while the nitrous acid scavenger is hydrazinium nitrate, also called hydrazine.
- an operation whose purpose is to complete the back-extraction of plutonium from the solvent phase by means of an aqueous nitric phase, also of low acidity and containing uranous nitrate and hydrazine; and
- an operation whose purpose is to back-extract the uranium(VI) from said solvent phase by means of a very dilute aqueous nitric solution.

[0012] Since the back-extraction of the plutonium from the solvent phase is accompanied by partial back-extraction of the uranium, the partition further includes a step whose purpose is to remove the uranium from the aqueous nitric phase resulting from the operation of back-extracting the plutonium by means of a solvent phase, of the same composition as that used for coextracting the uranium and plutonium.

[0013] Thus, what are obtained after the first cycle are:

- * a first aqueous stream that contains more than 99% of the plutonium initially present in the dissolution liquor and no longer contains any uranium; and
- * a second aqueous stream that contains more than 99% of the uranium initially present in the dissolution

liquor and no longer contains any plutonium.

[0014] The first aqueous stream resulting from the first cycle is then subjected to the "*second plutonium cycle*", the purpose of which is to complete the decontamination of the plutonium from the fission products liable to be still present in trace amounts in this stream. Thereafter, this stream which contains plutonium at a purity level of greater than 99.9%, is directed to a zone where the plutonium is converted into the oxide (PuO_2) and then stored in this form, for the purpose of its subsequent use in the manufacture of MOX nuclear fuel pellets.

[0015] In parallel, the second aqueous stream resulting from the first cycle is subjected to the "*second uranium cycle*", the purpose of which is to complete the decontamination of the uranium from the fission products, but especially to separate it from the neptunium.

[0016] This is because, in the first cycle, most of the neptunium present in the dissolution liquor is extracted, mainly in the form of neptunium(VI) at the same time as the uranium and the plutonium. During the reducing back-extraction of the plutonium in the first cycle, the neptunium(VI) is reduced by uranous nitrate to neptunium(IV), in which state it can be extracted by TBP, although less than in oxidation state (VI).

[0017] The neptunium therefore almost quantitatively follows the uranium during all the operations of the first cycle, hence the need to subject the aqueous uranium-laden stream, resulting from the partition, to a complementary cycle suitable for stripping it of the neptunium before it is converted to uranium oxide.

[0018] Like the plutonium resulting from the "*second plutonium cycle*", the uranium has, after the "*second uranium cycle*", a purity level of greater than 99.9%. It is also converted to the oxide and stored in this form.

[0019] Moreover, a method has been proposed in United States Patent 4 278 559 for recycling spent nuclear fuels with the aim of limiting, in all the stages of this recycling, the risk of plutonium being diverted for military purposes.

[0020] This method is designed to obtain, after the step of coextracting, the uranium and plutonium in a solvent phase containing, apart from these elements, 0.1 to 10% of the fission products initially present in the dissolution liquor, then to obtain, during the partition step, a plutonium production stream diluted with uranium and containing most of the radioactive fission products present in said solvent phase. This plutonium production stream is then processed by a sol-gel method in order to obtain plutonium-uranium-fission products mixed oxide, which are subsequently used to manufacture fresh nuclear fuels.

[0021] Although the presence of radioactive fission products in non-negligible quantities in fresh nuclear fuels is not an obstacle to the use of these fuels in fast neutron reactors, this is not the case as regards their use in the current light-water reactors. This is because such a use would make it necessary to develop a new type of

fuel having a substantially increased content of fissile material because of the neutron-absorbing character of certain fission products and to carry out lengthy and expensive studies in order to obtain homologation of this fuel.

[0022] Moreover, the presence of radioactive fission products at all stages in the spent fuel reprocessing and fresh fuel production chains, as provided in the method described in US-A-4 278 559, means having installations provided with radiation protection systems suitable for processing radioactive streams, and this being the case for each of the plants involved in this chain. Implementation of this method on an industrial scale would therefore necessarily involve either substantial reinforcement of the radiological protection with which existing nuclear fuel reprocessing and production installations are provided, or the production of new installations especially designed for operating a highly radioactive processing chain, which in both cases would result in a very considerable overcost.

[0023] With a view to developing new plants for reprocessing spent nuclear fuel, the inventors were set the objective of providing a process which, like the PUREX process previously described, allows uranium and plutonium to be effectively decontaminated from the other chemical elements present in a spent nuclear fuel, and in particular from the fission products, but which, unlike the PUREX process, at no time leaves plutonium by itself, whether in the solid or liquid state.

[0024] The inventors were also set the objective that this process should make it possible to obtain a mixed uranium-plutonium oxide that can be directly used for the manufacture of MOX nuclear fuels, whatever the purpose of these fuels: namely fast neutron reactors or light-water reactors.

[0025] They were furthermore set the objective that this process should use, at least in part, the knowledge and know-how acquired in the PUREX process, in terms of both procedures and installations, so that it can be industrially exploited in the short or medium term.

SUMMARY OF THE INVENTION

[0026] These objectives, and yet others, are achieved by a process for reprocessing a spent nuclear fuel and of preparing a mixed uranium-plutonium oxide, which comprises at least:

- a) a step of separating the uranium and plutonium from the fission products, the americium and the curium that are present in an aqueous nitric solution that results from dissolving the spent nuclear fuel in nitric acid, this step comprising at least one operation of coextracting uranium, in oxidation state (VI), and plutonium, in oxidation state (IV), from said aqueous solution by bringing this solution into contact with a water-immiscible solvent phase containing at least one extractant;

- b) a step of partitioning the uranium and plutonium coextracted in step a) into two aqueous phases, namely a first aqueous phase containing plutonium and uranium, and a second aqueous phase containing uranium but not containing plutonium;
- c) a step of purifying the plutonium and uranium present in the first aqueous phase obtained after step b) from the fission products also liable to be found in this phase; and
- d) a step of coconverting the plutonium and uranium that are present in the aqueous phase obtained after step c) into a mixed uranium-plutonium oxide.

[0027] Thus, unlike the PUREX process described above, which provides, once the uranium and the plutonium have been coextracted from the dissolution liquor, for the complete separation of these two elements from each other, and subsequently processes them independently of each other, the process of the invention itself proposes to only partially separate the plutonium from the uranium and to keep it, throughout all the consecutive steps of this separation, in the presence of uranium until a mixed uranium-plutonium oxide is obtained.

[0028] Preferably, step a) of the process of the invention includes, in addition to a coextraction operation, at least one scrubbing operation carried out on the solvent phase obtained after this coextraction in order to remove from this phase the fission products that were extracted together with the uranium(VI) and the plutonium(IV), this scrubbing operation being performed by bringing said solvent phase into contact with an aqueous nitric phase.

[0029] Also preferably, step b) of the process of the invention comprises at least:

- b₁) a step of back-extracting the plutonium, in oxidation state (III), and a fraction of the uranium, in oxidation state (VI), which are present in the solvent phase obtained after step a), by bringing this phase into contact with an aqueous nitric phase containing a reducing agent capable of reducing plutonium(IV) to plutonium(III) without reducing the uranium, for example uranous nitrate (uranium(IV) nitrate) or hydroxylammonium nitrate; and
- b₂) an operation of back-extracting the uranium that has not been back-extracted from the solvent phase during operation b₁), by bringing this phase into contact with an aqueous nitric phase.

[0030] Two aqueous phases are thus obtained, one of which contains plutonium and uranium, while the other contains uranium but does not contain plutonium.

[0031] Step c) of the process of the invention then preferably comprises, at least:

- c₁) an operation of coextracting the plutonium, in oxidation state (IV), and the uranium, in oxidation state (VI), from the aqueous phase obtained after step b₁), by bringing this phase into contact with a water-im-

miscible solvent phase containing at least one extractant in an organic diluent;

c₂) a scrubbing operation in which the solvent phase obtained after operation c₁) is scrubbed in order to remove the fission products from this phase that were extracted together with the plutonium(IV) and the uranium(VI) during operation c₁), this scrubbing operation being performed by bringing this phase into contact with an aqueous nitric phase; and

c₃) an operation of back-extracting the plutonium, in oxidation state (III), and a fraction of the uranium, in oxidation state (VI), from the solvent phase obtained after operation c₂), by bringing this phase into contact with an aqueous nitric phase containing a reducing agent capable of reducing the plutonium(IV) to plutonium(III) without reducing the uranium, for example uranous nitrate or hydroxylammonium nitrate.

[0032] It goes without saying that, if steps b) and c) are carried out in the manner that has just been described, then the process of the invention further includes, between these steps, an oxidation operation in order to reoxidize the plutonium(III) present in the aqueous phase obtained after operation b₁) to plutonium (IV). This oxidation operation also allows the uranium(IV) also liable to be present in this phase to be reoxidized to uranium (VI) especially if the reducing agent used during operation b₁) is uranous nitrate.

[0033] Moreover, if step b) is carried out in the manner as just described, the aqueous phase obtained after operation b₁) inevitably contains neptunium.

[0034] It is therefore necessary to remove the latter if it is desired to obtain, at step d), a mixed uranium-plutonium oxide containing no neptunium.

[0035] Therefore, in one embodiment mode of the process according to the invention it includes the removal of the neptunium present in the aqueous phase obtained after operation b₁), either during step b) or during step c).

[0036] This removal of the neptunium may, firstly, be carried out by adding to step b) an operation b₃) of re-extracting the neptunium, in oxidation state (IV), from the aqueous phase obtained after operation b₁), by bringing this phase into contact with a water-immiscible solvent phase containing at least one extractant in an organic diluent.

[0037] Since uranium(VI) and neptunium(IV) behave in a relatively similar manner, a fraction of the uranium (VI) present in the aqueous phase obtained after operation b₁) is back-extracted with the neptunium. Therefore, the invention provides the possibility of adding the uranium either to the aqueous nitric phase subjected to operation b₃), or to the aqueous nitric phase subjected to operation c₃), or to both, if it is deemed necessary for these phases to be recharged with uranium.

[0038] In all cases, the uranium added may be uranium (VI) or uranium (IV).

[0039] The removal of the neptunium may also be carried out during operation c₂) by adding, to the aqueous

phase used during this operation, a reducing agent capable of selectively reducing neptunium(VI) to neptunium(V) that is to say without reducing the plutonium or the uranium, and to do so in order to allow the neptunium to pass into the aqueous phase while leaving the plutonium and the uranium in the solvent phase.

[0040] As a variant of the above it is also possible not to remove the neptunium present in the aqueous phase obtained after operation b₁) but to let it follow the plutonium present in this phase as far as step d), so as to obtain a mixed uranium-plutonium-neptunium oxide.

[0041] Therefore, depending on whether or not the neptunium present in the aqueous phase obtained after operation b₁) is removed, depending on the way in which this removal is carried out, depending on the type of reducing agent used during operation c₃) and depending on whether or not the uranium(IV) is added during this operation, there is obtained, after step c), an aqueous phase that contains plutonium(III), uranium(VI) and possibly also contains uranium(IV) and/or neptunium(IV) or (V).

[0042] However, in all cases, the aqueous phase obtained after step c) preferably does not contain more than one μCi of fission products per gram of plutonium so as to meet the NF ISO 13463 standard of June 2000 relating to the manufacture of MOX nuclear fuels for light-water reactors. Moreover, this aqueous phase advantageously has a U/Pu mass ratio ranging from about 20/80 to 50/50. Thus, the function of step c) is twofold: namely to purify the plutonium and uranium that are present in the first aqueous phase obtained after step b) with respect to the fission products, on the one hand, and to allow the uranium/plutonium mass ratio to be adjusted on the other hand.

[0043] Step d) itself is preferably carried out as described in French Patent Application No. 2 870 841, that is to say:

* by stabilizing the plutonium, in oxidation state (III), the uranium, in oxidation state (IV), and, where appropriate, the neptunium, in oxidation state (IV), by a singly-charged cation consisting only of atoms chosen from oxygen, carbon, nitrogen and hydrogen atoms, such as the hydrazinium cation;

* by coprecipitating the thus stabilized plutonium, uranium and, where appropriate, neptunium by oxalic acid or by one of its salts or of its derivatives; and then

* by calcining the resulting coprecipitate, preferably in an inert or very slightly oxidizing gas, for example a gas containing predominantly argon, in order to remove the carbon and prevent the formation of U_3O_8 .

[0044] In accordance with the invention, the process advantageously also includes a storage step, which consists in storing either the aqueous phase obtained after operation c₃) before step d) is carried out, or the mixed

uranium-plutonium oxide obtained after step d).

[0045] This storage step, which advantageously corresponds to several months of reprocessing spent nuclear fuels by the process of the invention, for example about 4 to 6 months, makes it possible, on the one hand, to ensure that the workshops responsible for reprocessing spent nuclear fuel are decoupled from those responsible for manufacturing fresh nuclear fuel from the mixed uranium-plutonium oxide obtained after this reprocessing, and on the other hand, to adjust the isotopy of the plutonium to that required by the workshops for manufacturing fresh nuclear fuel.

[0046] By means of the fact that plutonium, uranium and neptunium are more stable in solution in the oxidized state than in the reduced state, but that their coconversion to a mixed oxide requires them to be in the reduced state, the process of the invention provides, in the case of the aqueous phase obtained after step c₃) being stored, for this phase to be subjected:

* between step c) and the storage step, to an oxidation operation in order to reoxidize the plutonium(III) and, where appropriate, the uranium(IV) and/or the neptunium(IV) or (V) to plutonium(IV), to uranium(VI) and to neptunium(VI), respectively, and then to a concentration operation in order to reduce the volume of material stored; and

* between the storage step and step d):

* to a reduction operation, for example of the electrolytic type, in order to reduce the plutonium(IV), the uranium(VI), and, where appropriate, the neptunium(VI) to plutonium(III), to uranium(IV) and to neptunium(IV), respectively; or else

* to a reduction operation, for example by U(IV) or NHA, in which the plutonium(IV), and, where appropriate, the neptunium(VI), are reduced to plutonium(III) and neptunium(IV), respectively, in which case this reduction operation is supplemented with an operation of extracting the uranium(VI), by bringing said aqueous phase into contact with a water-immiscible solvent phase containing at least one extractant in an organic diluent.

[0047] In all cases, the process of the invention makes it possible to obtain a mixed uranium-plutonium oxide which, depending on whether or not the neptunium present in the aqueous phase after operation b₁) has been removed, contains no neptunium or, on the contrary, also contains neptunium.

[0048] In either case, this mixed oxide, which is in the form of a powder, can then be used directly for the manufacture of pellets of a mixed nuclear fuel.

[0049] For this manufacture, this mixed oxide preferably has a U/Pu mass ratio of around 50/50 when it does not contain neptunium and a U/Pu/Np mass ratio of around 49/49/2 when it does contain neptunium.

[0050] The parameters used during the various oper-

ations of the process of the invention such as the volume ratios of the solvent phases to the aqueous phases, the number and the duration of the contacting operations between these phases, the acidity of the aqueous phases, etc., and also the amounts of U(VI) or (IV) that can be added during operations b_1) and c_3), are therefore adjusted accordingly.

[0051] As a person skilled in the art will have understood on reading the foregoing text, the extractant for the solvent phases which is used in steps a) and c) and also during the uranium(VI) extraction operation prior to step d), is preferably chosen from extractants that complex the metallic species in oxidation states (IV) and (VI) more strongly than the metallic species in oxidation states (I), (II), (III) and (V), so that uranium(IV), uranium(VI), plutonium(IV), neptunium(IV) and neptunium(VI) are considerably more extractable than plutonium(III) and neptunium(V).

[0052] This extractant may in particular be a trialkyl phosphate, such as tri-*n*-butyl phosphate (or TBP), triisobutyl phosphate (TiBP) or a triisoamyl phosphate.

[0053] The organic diluent for this extractant may itself be chosen from various hydrocarbons proposed for liquid-liquid extractions, such as toluene, xylene, *t*-butylbenzene, triisopropylbenzene, kerosene and linear or branched dodecanes, such as *n*-dodecane or hydrogenated tetrapropylene (HPT).

[0054] However, it is preferred to use, as in the PUREX process, tri-*n*-butyl phosphate in a dodecane, and to do so in a volume ratio of around 30/70.

[0055] As mentioned above, the reducing agent capable of reducing plutonium(IV) to plutonium(III), which is used during operations b_1) and c_3), may especially be uranous nitrate or hydroxylammonium nitrate. Preferably either one is used in conjunction with a nitrous acid scavenger, preferably hydrazine.

[0056] As regards the reducing agent capable of reducing neptunium(VI) to neptunium(V) without reducing either the uranium or the plutonium, which is used during operation c_2) for removing the neptunium, this may especially be a compound of the family of butyraldehydes or hydrazine.

[0057] In one particularly preferred embodiment mode of the process of the invention, when the uranium and plutonium are coextracted in step a) by means of a solvent phase containing about 30% (v/v) tri-*n*-butyl phosphate in a dodecane, this step comprises:

- a first scrubbing operation carried out on the solvent phase obtained after coextracting the uranium and plutonium, in order to remove most of the fission products, and in particular ruthenium and zirconium, which were extracted during this coextraction, by bringing said solvent phase into contact with an aqueous nitric phase containing around 1 to 3 mol/L of HNO_3 ;
- a second scrubbing operation carried out on the sol-

vent phase in order to remove, from this phase, the technetium which was extracted during the coextraction operation, by bringing said solvent phase into contact with an aqueous nitric phase containing around 3 to 5 mol/L of HNO_3 ; and

- a complementary operation of coextracting uranium and plutonium from the aqueous phase obtained after the second scrubbing operation, by bringing this phase into contact with a solvent phase containing about 30% (v/v) tri-*n*-butyl phosphate in a dodecane.

[0058] Moreover, in this particular preferred embodiment mode:

- * the aqueous nitric phases used during operations b_1) and c_3) contain around 0.05 to 2 mol/L of HNO_3 ;
- * the aqueous nitric phase used during operation b_2) contains around 0 to 0.05 mol/L of HNO_3 ; whereas
- * the aqueous nitric phase used during operation c_2) contains around 1 to 3 mol/L of HNO_3 .

[0059] If necessary, the process of the invention may also include operations of purifying the uranium present in the second aqueous phase obtained after step b), in order to complete its decontamination from the fission products and/or to separate it from the neptunium liable to have followed it in the aqueous phase during operation b_2). These operations may be carried out as in any conventional PUREX process (see, for example, the article BN 3 650 (07-2000) of the treatise "Genie Nucléaire" - "Techniques de l'Ingénieur").

[0060] The process according to the invention has many advantages. While being just as effective as the PUREX process in terms of decontamination, unlike the latter, it never allows plutonium to be left without uranium, and thus it minimizes the risk of plutonium being misappropriated for military purposes. It also makes it possible to obtain a mixed uranium-plutonium oxide powder that can be used directly for the manufacture of MOX nuclear fuels for fast neutron reactors or light-water reactors of the second or third generation.

[0061] Moreover, it is equally applicable to the reprocessing of a spent uranium oxide nuclear fuel as to the reprocessing of a spent mixed uranium-plutonium oxide nuclear fuel.

[0062] Other advantages and features of the process of the invention will become apparent upon reading the rest of the description that follows, which refers to examples of processes for the industrial-scale implementation of this process.

[0063] Of course, these examples are given merely to illustrate the invention and in no way constitute a limitation thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0064]

Figure 1 shows a block diagram of a first embodiment mode of the process of the invention.

Figure 2 shows a block diagram of a first variant of the embodiment mode illustrated in Figure 1.

Figure 3 shows a block diagram of a second variant of the embodiment mode illustrated in Figure 1.

Figure 4 shows a block diagram of a third variant of the embodiment mode illustrated in Figure 1.

Figure 5 shows a block diagram of a second embodiment mode of the process according to the invention.

[0065] In the embodiments modes shown in Figures 1 to 5, all the extraction, back-extraction and re-extraction operations are carried out in multi-staged units of the mixer/settler, pulsed column or centrifuge-extractor type. The directions of flow of the solvent phase entering or leaving these units are shown symbolically by a continuous double-line arrow, while the directions of flow of the aqueous phase entering or leaving the said units are shown symbolically by a continuous single-line arrow.

DETAILED DESCRIPTION OF EMBODIMENT MODES OF THE PROCESS ACCORDING TO THE INVENTION

[0066] The description firstly refers to Figure 1, which shows a block diagram of a first embodiment mode of the process of the invention, designed to obtain a mixed uranium-plutonium oxide powder containing no neptunium and able to be used directly in the manufacture of an MOX nuclear fuel, from a dissolution liquor of a spent UO_2 nuclear fuel that has been conventionally prepared, that is to say by dissolving this fuel in nitric acid and clarifying the resulting mixture.

[0067] Such a dissolution liquor typically contains 200 to 300 g/L of uranium per 2 to 3 g/L of plutonium, i.e. a U/Pu ratio of about 100/1, and has a content of fission products of around 50 to 70 Ci per gram of plutonium.

[0068] As mentioned previously, the process of the invention firstly comprises a step designed to separate the uranium and the plutonium from the fission products, the americium and the curium.

[0069] As may be seen in Figure 1, this separation step comprises:

* an operation, labelled "*U/Pu coextraction*", which consists in extracting both the uranium and the plutonium, the first in oxidation state (VI), the second in oxidation state (IV), from the dissolution liquor by bringing this liquor into contact with a solvent phase containing about 30% (v/v) tri-n-butyl phosphate (TBP) in an organic diluent, for example, a dodecane;

* an operation, labelled "*FP s.crubbing*", which consists in removing from the solvent phase the fission products, particularly ruthenium and zirconium, that have been extracted during the "*U/Pu coextraction*" by bringing the solvent phase resulting from this co-extraction into contact with an aqueous nitric phase of moderate acidity, for example a 1 to 3M nitric acid solution;

* an operation, labelled "*Tc scrubbing*", which consists in removing from the solvent phase the technetium that has been extracted during the "*U/Pu coextraction*", by bringing the solvent phase resulting from the "*FP scrubbing*" into contact with an aqueous nitric phase of moderate acidity, but higher than that of the aqueous nitric phase used for the "*FP scrubbing*", for example a 3M to 5M nitric acid solution; and

* an operation, labelled "*U/Pu complementary coextraction*", which consists in recovering the U(VI) and Pu(IV) fractions that have followed the technetium in the aqueous phase during the "*Tc scrubbing*", by bringing this aqueous phase into contact with a solvent phase, again consisting of about 30% (v/v) TBP in a dodecane.

[0070] Four phases are thus obtained:

- the two aqueous phases (or raffinates) resulting from the "*U/Pu coextraction*" and from the "*U/Pu complementary coextraction*", which are laden with fission products and, in the case of the first of said aqueous phases, with americium and with curium, and which are removed from the process;
- the solvent phase resulting from the "*U/Pu complementary coextraction*" which is sent to the unit where the "*U/Pu coextraction*" takes place, to be added to the solvent phase flowing through this unit; and
- the solvent phase resulting from the "*Tc scrubbing*" which is laden with U(VI), with Pu(IV) but also with neptunium(VI) (since most of the neptunium present in the dissolution liquor is extracted by the TBP) and is sent to a zone where the uranium/plutonium partition step takes place, in which two aqueous phases are formed, the first containing plutonium and uranium, the second phase containing uranium but no plutonium.

[0071] This partition step comprises:

- an operation, labelled "*Pu/U back-extraction*", which consists in back-extracting, from the solvent phase resulting from the "*Tc scrubbing*", the plutonium(IV) and a fraction of the uranium(VI) that are present in this phase, by bringing said solvent phase into contact with an aqueous phase of low acidity, for example a 0.05 to 2M nitric acid solution, containing a reducing agent that reduces the Pu(IV) to Pu(III) and neptunium(VI) to neptunium(IV), respectively, and to do so without reducing the uranium, and also a

nitrous acid scavenger suitable for destroying the nitrous acid that tends to form in the aqueous phase, and thus to stabilize the reducing agent and the Pu (III). This reducing agent is, for example, uranous nitrate (or U(IV)), whereas the nitrous acid scavenger is, for example, hydrazine (or NH₂);

- an operation, labelled "*Pu barrage*", which consists in completing the back-extraction of the plutonium (IV) by bringing the solvent phase resulting from the "*Pu/U back-extraction*" into contact with an aqueous nitric phase of low acidity, for example a 0.05 to 2M nitric acid solution, containing the same reducing agent and the same nitrous acid scavenger as those used for the "*Pu/U back-extraction*"; and
- an operation, labelled "*U back-extraction*" which consists in back-extracting the uranium(VI) from the solvent phase resulting from the "*Pu barrage*", by bringing this solvent phase into contact with a very dilute aqueous nitric phase, for example a 0 to 0.05M nitric acid solution.

[0072] Since neptunium(IV) is less extractable by TBP than neptunium(VI), it is partially back-extracted during the "*Pu/U back-extraction*". The aqueous phase resulting from this operation therefore contains neptunium in addition to plutonium and uranium.

[0073] The partition step therefore also includes an operation, labelled "*Np scrubbing*", which consists in back-extracting the neptunium(IV) present in the aqueous phase resulting from the "*Pu/U back-extraction*", by bringing this phase into contact with a solvent phase consisting of about 30% (v/v) TBP in a dodecane, in order to remove from this aqueous phase the neptunium fraction that it contains.

[0074] Moreover, since uranium(VI) and neptunium (IV) behave in a relatively similar manner, a fraction of the uranium(VI) present in the aqueous phase resulting from the "*U/Pu back-extraction*" is re-extracted with the neptunium, which fraction may be relatively large depending on the parameters used to carry out the "*Np scrubbing*".

[0075] Thus, and as may be seen in Figure 1, it is possible, according to the invention, to add uranium to the aqueous phase subjected to the "*Np scrubbing*", just before said phase leaves the unit where this operation takes place, in order to recharge this aqueous phase with uranium should this be deemed necessary. This uranium, which may without distinction be uranium(VI) or uranium (IV), may be added in the form of an aqueous nitric solution, it being understood that, if it is uranium(IV), the latter is then stabilized by a nitrous acid scavenger of the hydrazine type.

[0076] The aqueous phase resulting from the "*Np scrubbing*" is then subjected to an oxidation operation for bringing the Pu(III) back to oxidation state (IV) and, where appropriate, the U(IV) to oxidation state (VI), before the step of purifying the plutonium and the uranium that it contains is carried out.

[0077] This oxidation operation may especially be carried out in a conventional manner, that is to say by making said aqueous phase flow, after possibly being diluted with an aqueous nitric phase of high acidity, for example a 12M nitric acid solution, in a stream of nitrogen oxides NO_x so as to destroy the nitrous acid scavenger that it contains, thereby making it possible for the nitrous acid to reform and reoxidize the Pu(III) to Pu(IV), the excess nitrous acid then being removed by decomposition to NO and NO₂ and venting of the nitrogen oxides thus formed.

[0078] The step of purifying the plutonium and the uranium which follows the partition step and is for the purpose of completing the decontamination of these two elements from the fission products, i.e. so as to obtain in practice an aqueous plutonium-uranium stream preferably having a content of fission products of at most 1 µCi per gram of plutonium, comprises:

* an operation, labelled "*Pu/U coextraction*", which consists in jointly extracting the plutonium(IV) and the uranium(VI) from the aqueous phase resulting from the oxidation operation, by bringing this phase into contact with a solvent phase consisting of about 30% (v/v) TBP in a dodecane, as previously;

* an operation, labelled "*FP scrubbing*", which consists in removing from the solvent phase resulting from the "*Pu/U coextraction*" the fission products that have been extracted during this coextraction, by bringing this solvent phase into contact with an aqueous nitric phase of moderate acidity, for example a 1 to 3M nitric acid solution; and

* an operation, labelled "*U/Pu back-extraction*", which consists in back-extracting from the solvent phase resulting from the "*FP scrubbing*" the plutonium(IV) and a fraction of the uranium(VI) that are present in this phase, by bringing the latter into contact with an aqueous nitric phase of low acidity, for example a 0.05 to 2M nitric acid solution, containing a reducing agent capable of reducing the Pu(IV) to Pu(III), without touching the uranium, for example, hydroxylammonium nitrate (or HAN), stabilized by a nitrous acid scavenger of the hydrazine type.

[0079] As may be seen in Figure 1, it is possible, here again, to add uranium to the aqueous phase subjected to the "*U/Pu back-extraction*" just before the aqueous phase leaves the unit where this operation takes place, in order to recharge this aqueous phase with uranium should this be deemed necessary. As previously, the uranium thus added may be uranium(VI) or uranium(IV), as an aqueous nitric solution containing, in addition, a nitrous acid scavenger if the uranium is uranium(IV).

[0080] The raffinate resulting from the "*Pu/U coextraction*" is removed from the process.

[0081] The solvent phase resulting from the "*Pu/U back-extraction*", which contains uranium but no longer contains plutonium, rejoins the solvent phase resulting from the "*Np scrubbing*".

[0082] The aqueous phase resulting from the "*Pu/U back-extraction*", which is laden with purified plutonium (III) and uranium(IV) or (VI) is itself sent to a unit where, after an oxidation operation for reoxidizing the Pu(III) to Pu(IV) and which is preferably carried out in the same way as the oxidation operation following the "*Np scrubbing*", it is subjected to the concentration step in order to increase its plutonium content and its uranium content.

[0083] The aqueous phase thus concentrated is then stored, for example in tanks with a system of tubes, for a period advantageously corresponding to several months of implementation of the reprocessing process, for example 4 to 6 months, so as to have a stock of purified plutonium and uranium sufficient so that the workshops responsible for manufacturing MOX nuclear fuel are able to work independently of the workshops responsible for reprocessing the spent fuel. This storage also makes it possible to adjust the isotopy of the plutonium to that required for the workshops for manufacturing MOX nuclear fuel.

[0084] After the storage, the process of the invention further includes:

- an operation to reduce the plutonium(IV) present in the concentrated aqueous phase to Pu(III) by the addition of an aqueous nitric solution containing U (IV) stabilized by a nitrous acid scavenger; and
- an operation, labelled "*U scrubbing*", which consists in removing from the concentrated aqueous phase the uranium(VI) that it contains by bringing this aqueous phase into contact with a solvent phase, again consisting of approximately 30% (v/v) TBP in a dodecane.

[0085] The solvent phase resulting from the "*U scrubbing*" rejoins the solvent phase resulting from the "*Pu/U back-extraction*" of the purification step and, with it, the solvent phase resulting from the "*Np scrubbing*".

[0086] The aqueous phase resulting from the "*U scrubbing*" is itself directed to a unit where, after a possible adjustment of its U(IV) content suitable for in this phase a U(Pu) mass ratio consistent with that which the mixed uranium-plutonium oxide that it is desired to prepare must have, the step of coconverting the plutonium and uranium to a mixed oxide is carried out.

[0087] As previously mentioned, this coconversion step is preferably carried out according to the process described in FR-A-2 870 841, that is to say by coprecipitation, by oxalic acid or one of its salts or one of its derivatives of uranium(IV) and plutonium(III) that had been prestabilized by a singly charged cation consisting only of atoms chosen from oxygen, carbon, nitrogen and hydrogen atoms, such as the hydrazinium cation, or by a compound such as a salt, capable of forming such a cation, followed by calcination of the resulting coprecipitate, preferably in an inert or very slightly oxidizing gas, for example a gas containing predominantly argon.

[0088] The mixed uranium-plutonium oxide powder

thus obtained can then be used to manufacture MOX nuclear fuel pellets, for example by a MIMAS process, in which case this powder is screened, mixed with uranium oxide and possibly with scrap from the manufacture of pellets in the form of chamotte, and then the resulting mixture undergoes a pelletizing operation followed by a sintering operation.

[0089] As indicated above, it is preferred to use, for the manufacture of MOX nuclear fuels, a mixed oxide powder having a U/Pu mass ratio of approximately 50/50.

[0090] Consequently, the amounts of uranium that is introduced into the unit where the "*Np scrubbing*" takes place is preferably such that the aqueous phase resulting from this operation has a U/Pu mass ratio of around 20/80 to 50/50, and the parameters used to carry out the "*Pu/U back-extraction*" located downstream of this "*Np scrubbing*" are preferably adjusted so as to obtain, after this back-extraction, an aqueous phase having a U/Pu mass ratio of around 20/80 to 50/50 and, ideally, of around 20/80 to 30/70. It is desirable to obtain such a ratio in order to minimize the volume of material stored in tanks.

[0091] In any case, by adjusting the U(IV) content of the aqueous phase resulting from the "*U scrubbing*" it is possible, should it be necessary, to give the aqueous phase subjected to the co-conversion operation a U/Pu ratio equal or approximately equal to 50/50.

[0092] In the embodiment mode of the process of the invention illustrated in Figure 1, this includes, in addition, operations of purifying the uranium present in the aqueous phase resulting from the "*U back-extraction*", which operations are intended to complete its decontamination from the fission products and most particularly to separate it from the neptunium fraction that had followed it during the "*Pu/U back-extraction*" and the "*U back-extraction*" of the partition step. These purification operations may be carried out as in any conventional PUREX process and have consequently not been shown in Figure 1 for the sake of simplifying this figure, nor have they been shown in the following figures.

[0093] The process of the invention may also include ancillary operations, in particular operations of scrubbing, with pure diluent, the aqueous phases intended to be sent to the vitrification unit and operations of scrubbing and regenerating the spent solvent phases. Here again, these operations, which are well known in the prior art, have not been shown in Figures 1 to 5 for the sake of simplifying these figures.

[0094] A block diagram of a first variant of the embodiment mode illustrated in Figure 1 will now be described with reference to Figure 2, in which:

- the partition step does not include "*Np scrubbing*"; and
- the neptunium present in the aqueous phase resulting from the "*Pu/U back-extraction*" of this step is removed during the purification step.

[0095] To do this, after a "*Pu/U coextraction*" operation

similar to that of the embodiment mode described above, the "*FP scrubbing*" of the purification step is carried out by bringing the solvent phase resulting from this coextraction into contact with an aqueous phase of moderate acidity, for example a 1 to 3M aqueous nitric acid solution, to which has been added a reducing agent capable of reducing neptunium(VI) which is extractable by TBP, to neptunium(V), which is not extractable by TBP, and to do so without reducing either the plutonium or the uranium. This reducing agent is, for example, a butyraldehyde (ButAl).

[0096] The neptunium thus passes into the aqueous phase, whereas the plutonium and the uranium remain in the solvent phase.

[0097] The "*Pu/U back-extraction*" is then carried out in the mode of implementation described above, but by suitably adjusting the parameters of this operation so as to obtain a U/Pu mass ratio of around 20/80 to 50/50 and, ideally, of around 20/80 to 30/70 in the aqueous phase, bearing in mind that the U/Pu mass ratio of the solvent phase resulting from the "*FP scrubbing*" is likely to be almost the reverse because of the absence of "*Np scrubbing*".

[0098] Figure 3 shows a block diagram of a second variant of the embodiment mode illustrated in Figure 1.

[0099] This second variant differs from the variant that has just been described in that the reducing agent present in the aqueous phase used during the "*Pu/U back-extraction*" and "*Pu barrage*" operations of the partition step is an agent that is capable of reducing plutonium(IV) to plutonium(III) and neptunium(VI) to neptunium(V), respectively, this being the case, for example, of hydroxylammonium nitrate.

[0100] Since neptunium(V) is not extractable by TBP, it is therefore completely back-extracted during the "*Pu/U back-extraction*" and the "*Pu barrage*" and what are obtained after the partition step are two aqueous phases, one of which, resulting from the "*Pu/U back-extraction*" contains plutonium, uranium, and neptunium, whereas the other, resulting from the "*U back-extraction*" contains uranium but does not contain either plutonium or neptunium.

[0101] The removal of the neptunium present in the aqueous phase resulting from the "*U/Pu back-extraction*" of the partition step is then carried out during the "*FP scrubbing*" of the purification step, in exactly the same way as in the first variant.

[0102] This variant makes it possible, in the case of reprocessing spent nuclear fuels that have cooled for about 10 years or more, to dispense with the operations intended to purify the uranium.

[0103] Figure 4 shows schematically yet another variant of the embodiment mode of the process of the invention illustrated in Figure 1, which differs from this embodiment mode in that the aqueous phase resulting from the "*Pu/U back-extraction*" of the purification step is sent directly to a unit where the step of coconverting the plutonium and uranium to a mixed oxide is carried out.

[0104] In this variant, the "*Pu/U back-extraction*" operation of the purification step therefore necessarily includes the addition of a suitable amount of uranium(IV) so as to give the aqueous phase resulting from this operation a U/Pu mass ratio consistent with that which the mixed uranium-plutonium oxide that it is desired to manufacture must have.

[0105] Moreover, the decoupling between the workshops responsible for manufacturing MOX nuclear fuel and the workshops responsible for reprocessing spent nuclear fuel is ensured by storing the mixed uranium-plutonium oxide powder obtained after the coconversion step.

[0106] Figure 5 illustrates schematically a second embodiment mode of the process of the invention which, unlike the previous ones, is designed to obtain a mixed uranium-plutonium oxide powder, which also contains neptunium, from a dissolution liquor of a spent UO₂ nuclear fuel.

[0107] In this embodiment mode, the process takes place as in the mode of implementation illustrated in Figure 3 except that it does not include the elimination of the neptunium during the "*FP scrubbing*" of the purification step.

[0108] The neptunium therefore accompanies the plutonium with which it was back-extracted during the "*Pu/U back-extraction*" throughout all the subsequent steps of the process until a mixed uranium-plutonium-neptunium oxide is obtained.

[0109] To give an example, a simulation was carried out using the PAREX Code of the Commissariat à l'Energie Atomique for the first embodiment mode of the process of the invention illustrated in Figure 1.

[0110] The data of this simulation were the following:

Dissolution liquor:

[0111]

[U] = 250 g/L
[Pu] = 2.55 g/L
4.5M HNO₃
Feed flow rate in the process = 637 L/h;

Solvent phases:

[0112] 30% (v/v) TBP in TPH;

Step of separating the uranium and plutonium from the fission products, americium and curium:

[0113]

- * Solvent phase entering the "*U/Pu coextraction*" unit: flow rate = 1272 L/h
- * Aqueous phase entering the "*FP scrubbing*" unit: 2M HNO₃, flow rate = 273 L/h
- * Aqueous phase entering the "*Tc scrubbing*" unit:

1.5M HNO₃, flow rate = 38 L/h; then 12M HNO₂, flow rate = 200 L/h.

* Solvent phase entering the "*U/Pu complementary coextraction*" unit: flow rate = 545 L/h;

Partition step, separating uranium and plutonium into two aqueous phases:

[0114]

* Aqueous phase entering the "*Pu barrage*" unit: 0.2M HNO₂ + 0.15M hydrazine, flow rate = 236 L/h;

then 0.2M HNO₃ 150 g/L U(IV), flow rate = 9.4 L/h

* Addition of U(IV) to the "*Pu/U back-extraction*" unit: 150 g/L, flow rate = 21.7 L/h

* Solvent phase entering the "*Np scrubbing*" unit: flow rate = 215 L/h

* Aqueous phase leaving the "*Np scrubbing*" unit:

[Pu] = 6 g/L

[U] = 1.83 g/L

Flow rate = 272.5 L/h;

Oxidation operation:

[0115]

* Aqueous phase used to dilute the aqueous phase resulting from the "*Np scrubbing*": 12M HNO₃, flow rate = 110 L/h

* Aqueous phase resulting from the oxidation operation:

[Pu] = 4.2 g/L

[U] = 1.3 g/L

Flow rate = 385.4 L/h;

Plutonium/uranium purification step:

[0116]

* Solvent phase entering the "*Pu/U coextraction*" unit: flow rate = 95 L/h

* Aqueous phase entering the "*FP scrubbing*" unit: 1.5M HNO₃, flow rate = 24 L/h; then 12M HNO₃, flow rate = 6 L/h

* Aqueous phase entering the "*Pu/U back-extraction*" unit: 0.2M HNO₃ + 0.2M hydrazine + 0.4M hydroxylammonium nitrate, flow rate = 47 L/h

* Addition of U(IV) to the "*Pu/U back-extraction*" unit: 150 g/L, flow rate = 11 L/h

* Aqueous phase leaving the "*Pu/U back-extraction*" unit:

[Pu] = 27.5 g/L

[U] = 6.7 g/L

Flow rate = 59.1 L/h;

Concentration step:

[0117] Aqueous phase resulting from the concentra-

tion operation:

[Pu] = 200 g/L

[U] = 50 g/L;

5 Reduction operation:

[0118]

* Addition of U(IV) to the reduction unit: 200 g/L, flow rate = 8.1 L/h

* Aqueous phase resulting from the reduction operation:

[Pu] = 100 g/L

[U] = 125 g/L; and

15 Adjustment operation

[0119] Aqueous phase adjustment: HNO₃ + 200 g/L U (IV).

20 What is thus obtained is an aqueous phase containing 50 g/L of Pu, in oxidation state (III), and 50 g/L of U, in oxidation state (IV), which have a purity level of greater than 99% and are suitable for being coconverted to a mixed uranium-plutonium oxide.

25 CITED REFERENCES

[0120]

30 US-A-4 278 559

FR-A-2 870 841

Article BN 3650 (07-2000): The treatise "Genie Nucléaire" - "Techniques de l'Ingénieur".

35 Claims

1. Process for reprocessing a spent nuclear fuel and of preparing a mixed uranium-plutonium oxide, which comprises at least:

a) a step of separating the uranium and plutonium from the fission products, the americium and the curium that are present in an aqueous nitric solution that results from dissolving the spent nuclear fuel in nitric acid, this step comprising at least one operation of coextracting uranium, in oxidation state (VI), and plutonium, in oxidation state (IV), from said aqueous solution by bringing this solution into contact with a water-immiscible solvent phase containing at least one extractant in an organic diluent;

b) a step of partitioning the uranium and plutonium coextracted in step a) into two aqueous phases, namely a first aqueous phase containing plutonium and uranium, and a second aqueous phase containing uranium but not containing plutonium;

- c) a step of purifying the plutonium and uranium present in the first Aqueous phase obtained after step b) from the fission products also liable to be found in this phase; and
 d) a step of coconverting the plutonium and uranium that are present in the aqueous phase obtained after step c) into a mixed uranium-plutonium oxide.
2. Process according to Claim 1, in which step a) also includes at least one scrubbing operating in which the solvent phase obtained after the uranium-plutonium coextraction operation is scrubbed by bringing this phase into contact with an aqueous nitric phase.
3. Process according to Claim 1 or Claim 2, in which:
- * step b) comprises at least:
- b₁) a step of back-extracting the plutonium, in oxidation state (III), and a fraction of the uranium, in oxidation state (VI), from the solvent phase obtained after step a), by bringing this phase into contact with an aqueous nitric phase containing a reducing agent capable of reducing plutonium(IV) to plutonium(III) without reducing the uranium; and
 b₂) an operation of back-extracting the uranium that has not been back-extracted from said solvent phase during operation b₁), by bringing this phase into contact with an aqueous nitric phase; whereas
- * step c) comprises at least:
- c₁) an operation of coextracting the plutonium, in oxidation state (IV), and the uranium, in oxidation state (VI), from the aqueous phase obtained after step b₁), by bringing this phase into contact with a water-immiscible solvent phase containing at least one extractant in an organic diluent;
 c₂) a scrubbing operation in which the solvent phase obtained after operation c₁) is scrubbed by bringing this phase into contact with an aqueous nitric phase; and
 c₃) an operation of back-extracting the plutonium, in oxidation state (III), and a fraction of the uranium, in oxidation state (VI), from the solvent phase obtained after operation c₂), by bringing this phase into contact with an aqueous nitric phase containing a reducing agent capable of reducing plutonium(IV) to plutonium(III) without reducing the uranium(VI).
4. Process according to Claim 3, which further includes, between steps b) and c), an operation of oxidizing the plutonium(III) present in the aqueous phase obtained after step b₁) to plutonium(IV).
5. Process according to Claim 3, in which, since neptunium is present in the aqueous phase obtained after step b₁), this neptunium is removed either during step b) or during step c).
6. Process according to Claim 5, in which, in order to remove the neptunium, step b) also includes an operation b₃) of re-extracting the neptunium, in oxidation state (IV), from the aqueous phase obtained after operation b₁), by bringing this phase into contact with a water-immiscible solvent phase containing at least one extractant in an organic diluent.
7. Process according to Claim 6, in which operation b₃) further includes the addition of uranium (VI) or (IV) to the aqueous nitric phase subjected to this operation.
8. Process according to Claim 6, in which operation c₃) further includes the addition of uranium (VI) or (IV) to the aqueous nitric phase subjected to this operation.
9. Process according to Claim 5, in which, in order to remove the neptunium, the aqueous nitric phase used during operation c₂) includes a reducing agent capable of reducing neptunium(VI) to neptunium(V) without reducing the plutonium(IV) or the uranium (VI).
10. Process according to Claim 3, in which, since neptunium is present in the first aqueous phase obtained after step b₁), this neptunium is left to follow the plutonium present in this phase up to step d).
11. Process according to any one of Claims 5 to 10, in which step d) comprises:
- the , stabilization of the plutonium, in oxidation state (III), of the uranium, in oxidation state (IV), and, where appropriate, of the neptunium, in oxidation state (IV), by a singly-charged cation consisting only of atoms chosen from oxygen, carbon, nitrogen and hydrogen atoms;
 - the coprecipitation of the thus stabilized plutonium, uranium and, where appropriate, neptunium by oxalic acid or by one of its salts or of its derivatives; and then
 - the calcination of the coprecipitate thus obtained.
12. Process according to any one of Claims 5 to 11, which further includes, between steps c) and d), a step of storing the aqueous phase obtained after operation c₃).

13. Process according to Claim 12, dependent on Claim 11, which further includes:

* between step c) and the storage step, an operation of oxidizing the plutonium(III) present in the aqueous phase obtained after operation c_3) to plutonium(IV), followed by an operation of concentrating this aqueous phase; and
 * between the storage step and step d), an operation of reducing the plutonium(IV), the uranium(VI) and, where appropriate, the neptunium(VI), which are present in the concentrated aqueous phase that has been stored, to plutonium(III), to uranium(IV) and to neptunium(IV).

14. Process according to Claim 12, dependent on Claim 11, which further includes:

*) between step c) and the storage step, an operation of oxidizing the plutonium(III) present in the aqueous phase obtained after operation c_3) to plutonium(IV), followed by an operation of concentrating this aqueous phase; and
 *) between the storage step and step d), an operation of reducing the plutonium(IV), and, where appropriate, the neptunium(VI), which are present in the concentrated aqueous phase that has been stored, to plutonium(III), followed by an operation of extracting the uranium(VI), by bringing said aqueous phase into contact with a water-immiscible solvent phase containing at least one extractant in an organic diluent.

15. Process according to Claim 11, dependent on Claim 5, in which the mixed uranium-plutonium oxide obtained after step d) contains no neptunium.
 16. Process according to Claim 15, in which the mixed uranium-plutonium oxide has a U/Pu mass ratio of around 50/50.
 17. Process according to Claim 11, dependent on Claim 10, in which the mixed uranium-plutonium oxide obtained after step d) contains neptunium.
 18. Process according to Claim 17, in which the mixed uranium-plutonium oxide has a U/Pu/Np mass ratio of around 49/49/2.
 19. Process according to any one of Claims 1, 3, 6 and 14, in which the solvent phase contains tri-*n*-butyl phosphate in a dodecane, in a volume ratio of around 30/70.
 20. Process according to Claim 19, in which step a) comprises:

- a first scrubbing operation carried out on the

solvent phase obtained after coextracting the uranium and plutonium, by bringing said solvent phase into contact with an aqueous nitric phase containing around 1 to 3 mol/L of HNO_3 ;

- a second scrubbing operation carried out on the solvent phase, by bringing said solvent phase into contact with an aqueous nitric phase containing around 3 to 5 mol/L of HNO_3 ; and
- a complementary operation of coextracting uranium and plutonium from the aqueous phase obtained after the second scrubbing operation, by bringing this phase into contact with a solvent phase containing about 30% (v/v) tri-*n*-butyl phosphate in a dodecane.

Patentansprüche

1. Verfahren zur Wiederaufbereitung eines verbrauchten bzw. abgebrannten Kernbrennstoffs und zum Herstellen eines gemischten Uran-Plutonium-Oxids, welches wenigstens umfasst:

a) einen Schritt der Abtrennung des Urans und Plutoniums von den Spaltprodukten, dem Americium und dem Curium, welche in einer wässrigen salpetersauren Lösung vorhanden sind, die sich aus dem Auflösen des verbrauchten Kernbrennstoffs in Salpetersäure ergibt, wobei dieser Schritt wenigstens einen Arbeitsgang der gemeinsamen Extraktion von Uran, in der Oxidationsstufe (VI), und Plutonium, in der Oxidationsstufe (IV), aus der wässrigen Lösung durch Inkontaktbringen dieser Lösung mit einer mit Wasser nicht mischbaren Lösungsmittelphase, die wenigstens ein Extraktionsmittel in einem organischen Verdünnungsmittel enthält, umfasst;
 b) einen Schritt der Verteilung des in Schritt a) gemeinsam extrahierten Urans und Plutoniums in zwei wässrige Phasen, nämlich eine erste wässrige Phase, die Plutonium und Uran enthält, und eine zweiten wässrige Phase, die Uran enthält, aber Plutonium nicht enthält;
 c) einen Schritt der Reinigung des in der nach Schritt b) erhaltenen ersten wässrigen Phase vorhandenen Plutoniums und Urans von den Spaltprodukten, die auch in dieser Phase vorkommen können; und
 d) einen Schritt des gemeinsamen Umwandels des Plutoniums und Urans, welche in der nach Schritt c) erhaltenen wässrigen Phase vorhanden sind, in ein gemischtes Uran-Plutonium-Oxid.

2. Verfahren nach Anspruch 1, in welchem Schritt a) auch wenigstens einen Wascharbeitsgang einschließt, in welchem die nach dem Arbeitsgang der gemeinsamen Extraktion von Uran und Plutonium

erhaltene Lösungsmittelphase durch Inkontaktbringen dieser Phase mit einer wässrigen salpetersauren Phase gewaschen wird.

3. Verfahren nach Anspruch 1 oder Anspruch 2, in welchem:

* Schritt b) wenigstens umfasst:

b₁) einen Schritt der Rückextraktion des Plutoniums, in der Oxidationsstufe (III), und einer Fraktion des Urans, in der Oxidationsstufe (VI), aus der nach Schritt a) erhaltenen Lösungsmittelphase durch Inkontaktbringen dieser Phase mit einer wässrigen salpetersauren Phase, die ein Reduktionsmittel enthält, das Plutonium (IV) zu Plutonium (III) reduzieren kann, ohne das Uran zu reduzieren; und

b₂) einen Arbeitsgang der Rückextraktion des Urans, welches während des Arbeitsgangs b₁) nicht aus der Lösungsmittelphase rückextrahiert worden ist, durch Inkontaktbringen dieser Phase mit einer wässrigen salpetersauren Phase; wogegen

* Schritt c) wenigstens umfasst:

c₁) einen Arbeitsgang der gemeinsamen Extraktion des Plutoniums, in der Oxidationsstufe (IV), und des Urans, in der Oxidationsstufe (VI), aus der wässrigen Phase, die nach Schritt b₁) erhalten wird, durch Inkontaktbringen dieser Phase mit einer mit Wasser nicht mischbaren Lösungsmittelphase, die wenigstens ein Extraktionsmittel in einem organischen Verdünnungsmittel enthält;

c₂) einen Wascharbeitsgang, in welchem die nach dem Arbeitsgang c₁) erhaltene Lösungsmittelphase durch Inkontaktbringen dieser Phase mit einer wässrigen salpetersauren Phase gewaschen wird; und

c₃) einen Arbeitsgang der Rückextraktion des Plutoniums, in der Oxidationsstufe (III), und einer Fraktion des Urans, in der Oxidationsstufe (VI), aus der nach Arbeitsgang c₂) erhaltenen Lösungsmittelphase durch Inkontaktbringen dieser Phase mit einer wässrigen salpetersauren Phase, die ein Reduktionsmittel enthält, das Plutonium (IV) zu Plutonium (III) reduzieren kann, ohne das Uran (VI) zu reduzieren.

4. Verfahren nach Anspruch 3, welches außerdem zwischen den Schritten b) und c) einen Arbeitsgang des Oxidierens des in der nach Schritt b₁) erhaltenen wässrigen Phase vorhandenen Plutoniums (III) zu

Plutonium (IV) einschließt.

5. Verfahren nach Anspruch 3, in welchem, da Neptunium in der nach Schritt b₁) erhaltenen wässrigen Phase vorhanden ist, dieses Neptunium entweder während Schritt b) oder während Schritt c) entfernt wird.

6. Verfahren nach Anspruch 5, in welchem, um das Neptunium zu entfernen, der Schritt b) auch einen Arbeitsgang b₃) der Rückextraktion des Neptuniums, in der Oxidationsstufe (IV), aus der nach Arbeitsgang b₁) erhaltenen wässrigen Phase durch Inkontaktbringen dieser Phase mit einer mit Wasser nicht mischbaren Lösungsmittelphase, die wenigstens ein Extraktionsmittel in einem organischen Verdünnungsmittel enthält, einschließt.

7. Verfahren nach Anspruch 6, in welchem der Arbeitsgang b₃) außerdem die Zugabe von Uran (VI) oder (IV) zu der diesem Arbeitsgang unterworfenen wässrigen salpetersauren Phase einschließt.

8. Verfahren nach Anspruch 6, in welchem der Arbeitsgang c₃) außerdem die Zugabe von Uran (VI) oder (IV) zu der diesem Arbeitsgang unterworfenen wässrigen salpetersauren Phase einschließt.

9. Verfahren nach Anspruch 5, in welchem, um das Neptunium zu entfernen, die wässrige salpetersaure Phase, die während Arbeitsgang c₂) verwendet wird, ein Reduktionsmittel einschließt, das Neptunium (VI) zu Neptunium (V) reduzieren kann, ohne das Plutonium (IV) oder das Uran (VI) zu reduzieren.

10. Verfahren nach Anspruch 3, in welchem, da Neptunium in der nach Schritt b₁) erhaltenen ersten wässrigen Phase vorhanden ist, dieses Neptunium dem in dieser Phase vorhandenen Plutonium bis zu Schritt d) folgen gelassen wird.

11. Verfahren nach einem der Ansprüche 5 bis 10, in welchem Schritt d) umfasst:

- die Stabilisierung des Plutoniums, in der Oxidationsstufe (III), des Urans, in der Oxidationsstufe (IV), und gegebenenfalls des Neptuniums, in der Oxidationsstufe (IV), durch ein einfach geladenes Kation, das nur aus Atomen besteht, die aus Sauerstoff-, Kohlenstoff-, Stickstoff- und Wasserstoffatomen ausgewählt sind;
- die Kopräzipitation des so stabilisierten Plutoniums, Urans und gegebenenfalls Neptuniums durch Oxalsäure oder durch eines von ihren Salzen oder von ihren Derivaten; und dann
- die Calcinierung des so erhaltenen Kopräzipitats.

12. Verfahren nach einem der Ansprüche 5 bis 11, welches außerdem zwischen den Schritten c) und d) einen Schritt der Aufbewahrung der nach Arbeitsgang c₃) erhaltenen wässrigen Phase einschließt.

13. Verfahren nach Anspruch 12, abhängig von Anspruch 11, welches außerdem einschließt:

* zwischen Schritt c) und dem Aufbewahrungsschritt, einen Arbeitsgang der Oxidation des in der nach Arbeitsgang c₃) erhaltenen wässrigen Phase vorhandenen Plutoniums (III) zu Plutonium (IV), gefolgt von einem Arbeitsgang der Konzentration dieser wässrigen Phase; und

* zwischen dem Aufbewahrungsschritt und Schritt d) einen Arbeitsgang der Reduktion des Plutoniums (IV), des Urans (VI) und gegebenenfalls des Neptuniums (VI), welche in der konzentrierten wässrigen Phase vorhanden sind, die aufbewahrt wurde, zu Plutonium (III), zu Uran (IV) und zu Neptunium (IV).

14. Verfahren nach Anspruch 12, abhängig von Anspruch 11, welches außerdem einschließt:

*) zwischen Schritt c) und dem Aufbewahrungsschritt einen Arbeitsgang der Oxidation des in der nach Arbeitsgang c₃) erhaltenen wässrigen Phase vorhandenen Plutoniums (III) zu Plutonium (IV), gefolgt von einem Arbeitsgang der Konzentration dieser wässrigen Phase; und

*) zwischen dem Aufbewahrungsschritt und Schritt d) einen Arbeitsgang der Reduktion des Plutoniums (IV) und gegebenenfalls des Neptuniums (VI), welche in der konzentrierten wässrigen Phase vorhanden sind, die aufbewahrt wurde, zu Plutonium (III), gefolgt von einem Arbeitsgang der Extraktion des Urans (VI) durch Inkontaktbringen der wässrigen Phase mit einer mit Wasser nicht mischbaren Lösungsmittelphase, die wenigstens ein Extraktionsmittel in einem organischen Verdünnungsmittel enthält.

15. Verfahren nach Anspruch 11, abhängig von Anspruch 5, in welchem das nach Schritt d) erhaltene gemischte Uran-Plutonium-Oxid kein Neptunium enthält.

16. Verfahren nach Anspruch 15, in welchem das gemischte Uran-Plutonium-Oxid ein U/Pu-Massenverhältnis von ungefähr 50/50 aufweist.

17. Verfahren nach Anspruch 11, abhängig von Anspruch 10, in welchem das nach Schritt d) erhaltene gemischte Uran-Plutonium-Oxid Neptunium enthält.

18. Verfahren nach Anspruch 17, in welchem das gemischte Uran-Plutonium-Oxid ein U/Pu/Np-Massen-

verhältnis von ungefähr 49/49/2 aufweist.

19. Verfahren nach einem der Ansprüche 1, 3, 6 und 14, in welchem die Lösungsmittelphase Tri-*n*-butylphosphat in einem Dodecan in einem Volumenverhältnis von ungefähr 30/70 enthält.

20. Verfahren nach Anspruch 19, in welchem Schritt a) umfasst:

- einen ersten Wascharbeitsgang, der an der nach dem gemeinsamen Extrahieren des Urans und Plutoniums erhaltenen Lösungsmittelphase durchgeführt wird, durch Inkontaktbringen der Lösungsmittelphase mit einer wässrigen salpetersauren Phase, die ungefähr 1 bis 3 mol/l HNO₃ enthält;
- einen zweiten Wascharbeitsgang, der an der Lösungsmittelphase durchgeführt wird, durch Inkontaktbringen der Lösungsmittelphase mit einer wässrigen salpetersauren Phase, die ungefähr 3 bis 5 mol/l HNO₃ enthält; und
- einen komplementären Arbeitsgang des gemeinsamen Extrahierens von Uran und Plutonium aus der nach dem zweiten Wascharbeitsgang erhaltenen wässrigen Phase durch Inkontaktbringen dieser Phase mit einer Lösungsmittelphase, die ungefähr 30 % (Vol./Vol.) Tri-*n*-butylphosphat in einem Dodecan enthält.

Revendications

1. Procédé de retraitement d'un combustible nucléaire usé et de préparation d'un oxyde mixte d'uranium et de plutonium, qui comprend au moins :

- a) une étape de séparation de l'uranium et du plutonium des produits de fission, de l'américium et du curium présents dans une solution aqueuse nitrique résultant de la dissolution du combustible nucléaire usé dans de l'acide nitrique, cette étape comprenant au moins une opération de co-extraction de l'uranium, à l'état d'oxydation (VI), et du plutonium, à l'état d'oxydation (IV), de ladite solution aqueuse, par mise en contact de cette solution avec une phase solvant non miscible à l'eau et contenant au moins un extractant dans un diluant organique ;
- b) une étape de répartition de l'uranium et du plutonium co-extraits à l'étape a) en deux phases aqueuses, une première phase aqueuse contenant du plutonium et de l'uranium, et une deuxième phase aqueuse contenant de l'uranium mais ne contenant pas de plutonium ;
- c) une étape de purification du plutonium et de l'uranium présents dans la première phase aqueuse obtenue à l'issue de l'étape b) vis-à-

- vis des produits de fission susceptibles de se trouver également dans cette phase ; et
d) une étape de co-conversion du plutonium et de l'uranium présents dans la phase aqueuse obtenue à l'issue de l'étape c) en un oxyde mixte d'uranium et de plutonium.
2. Procédé selon la revendication 1, dans lequel l'étape a) comprend, de plus, au moins une opération de lavage de la phase solvant obtenue à l'issue de l'opération de co-extraction de l'uranium et du plutonium, par mise en contact de cette phase avec une phase aqueuse nitrique.
3. Procédé selon la revendication 1 ou la revendication 2, dans lequel :
- * l'étape b) comprend au moins :
- b₁) une opération de dés extraction du plutonium, à l'état d'oxydation (III), et d'une fraction de l'uranium, à l'état d'oxydation (VI), de la phase solvant obtenue à l'issue de l'étape a), par mise en contact de cette phase avec une phase aqueuse nitrique contenant un agent réducteur capable de réduire le plutonium(IV) en plutonium(III) sans réduire l'uranium ; et
b₂) une opération de dés extraction de l'uranium n'ayant pas été dés extrait de ladite phase solvant au cours de l'opération b₁), par mise en contact de cette phase avec une phase aqueuse nitrique ; tandis que
- * l'étape c) comprend au moins :
- c₁) une opération de co-extraction du plutonium, à l'état d'oxydation (IV), et de l'uranium, à l'état d'oxydation (VI), de la phase aqueuse obtenue à l'issue de l'étape b₁), par mise en contact de cette phase avec une phase solvant non miscible à l'eau et contenant au moins un extractant dans un diluant organique ;
c₂) une opération de lavage de la phase solvant obtenue à l'issue de l'opération c₁) , par mise en contact de cette phase avec une phase aqueuse nitrique ; et
c₃) une opération de dés extraction du plutonium, à l'état d'oxydation (III), et d'une fraction de l'uranium, à l'état d'oxydation (VI), de la phase solvant obtenue à l'issue de l'opération c₂) , par mise en contact de cette phase avec une phase aqueuse nitrique contenant un agent réducteur capable de réduire le plutonium(IV) en plutonium(III) sans réduire l'uranium(VI).
4. Procédé selon la revendication 3, qui comprend, de plus, entre les étapes b) et c), une opération d'oxydation du plutonium(III) présent dans la phase aqueuse obtenue à l'issue de l'étape b₁) en plutonium(IV).
5. Procédé selon la revendication 3, dans lequel, du neptunium étant présent dans la phase aqueuse obtenue à l'issue de l'étape b₁), on élimine ce neptunium soit au cours de l'étape b), soit au cours de l'étape c).
6. Procédé selon la revendication 5, dans lequel, pour l'élimination du neptunium, l'étape b) comprend, de plus, une opération b₃) de ré-extraction du neptunium, à l'état d'oxydation (IV), de la phase aqueuse obtenue à l'issue de l'opération b₁), par mise en contact de cette phase avec une phase solvant non miscible à l'eau et contenant au moins un extractant dans un diluant organique.
7. Procédé selon la revendication 6, dans lequel l'opération b₃) comprend, de plus, l'ajout d'uranium(VI) ou (IV) à la phase aqueuse nitrique soumise à cette opération.
8. Procédé selon la revendication 6, dans lequel l'opération c₃) comprend, de plus, l'ajout d'uranium(VI) ou (IV) à la phase aqueuse nitrique soumise à cette opération.
9. Procédé selon la revendication 5, dans lequel, pour l'élimination du neptunium, la phase aqueuse nitrique utilisée au cours de l'opération c₂) comprend un agent réducteur capable de réduire le neptunium(VI) en neptunium(V) sans réduire le plutonium(IV) ni l'uranium(VI).
10. Procédé selon la revendication 3, dans lequel, du neptunium étant présent dans la première phase aqueuse obtenue à l'issue de l'étape b₁), on laisse ce neptunium suivre le plutonium présent dans cette phase jusqu'à l'étape d) .
11. Procédé selon l'une quelconque des revendications 5 à 10, dans lequel l'étape d) comprend :
- la stabilisation du plutonium, à l'état d'oxydation (III), de l'uranium, à l'état d'oxydation (IV), et, le cas échéant, du neptunium, à l'état d'oxydation (IV), par un cation monochargé constitué uniquement d'atomes choisis parmi les atomes d'oxygène, de carbone, d'azote et d'hydrogène ;
 - la co-précipitation du plutonium, de l'uranium et, le cas échéant, du neptunium ainsi stabilisés, par de l'acide oxalique ou par l'un de ses sels ou de ses dérivés ; puis
 - la calcination du co-précipité ainsi obtenu.

12. Procédé selon l'une quelconque des revendications 5 à 11, qui comprend de plus, entre les étapes c) et d), une étape d'entreposage de la phase aqueuse obtenue à l'issue de l'opération c₃).

13. Procédé selon la revendication 12 dépendante de la revendication 11, qui comprend de plus :

* entre l'étape c) et l'étape d'entreposage, une opération d'oxydation du plutonium(III) présent dans la phase aqueuse obtenue à l'issue de l'opération c₃ en plutonium(IV), suivie d'une opération de concentration de cette phase aqueuse ; et

* entre l'étape d'entreposage et l'étape d), une opération de réduction du plutonium (IV), de l'uranium (VI) et, le cas échéant, du neptunium (VI) présents dans la phase aqueuse concentrée ayant été entreposée, en plutonium(III), en uranium(IV) et en neptunium(IV).

14. Procédé selon la revendication 12 dépendante de la revendication 11, qui comprend de plus :

* entre l'étape c) et l'étape d'entreposage, une opération d'oxydation du plutonium(III) présent dans la phase aqueuse obtenue à l'issue de l'opération c₃ en plutonium(IV), suivie d'une opération de concentration de cette phase, aqueuse ; et

* entre l'étape d'entreposage et l'étape d), une opération de réduction du plutonium(IV) et, le cas échéant, du neptunium(VI) présents dans la phase aqueuse concentrée ayant été entreposée, en plutonium (III), suivie d'une opération d'extraction de l'uranium(VI), par mise en contact de ladite phase aqueuse avec une phase solvant non miscible à l'eau et contenant au moins un extractant dans un diluant organique.

15. Procédé selon la revendication 11 dépendant de la revendication 5, dans lequel l'oxyde mixte d'uranium et de plutonium obtenu à l'issue de l'étape d) est exempt de neptunium.

16. Procédé selon la revendication 15, dans lequel l'oxyde mixte d'uranium et de plutonium présente un rapport massique U/Pu de l'ordre de 50/50.

17. Procédé selon la revendication 11 dépendant de la revendication 10, dans lequel l'oxyde mixte d'uranium et de plutonium obtenu à l'issue de l'étape d) comprend du neptunium.

18. Procédé selon la revendication 17, dans lequel l'oxyde mixte d'uranium et de plutonium présente un rapport massique U/Pu/Np de l'ordre de 49/49/2.

19. Procédé selon l'une quelconque des revendications 1, 3, 6 etc 14, dans lequel la phase solvant contient du phosphate de tri-n-butyle dans un dodécane, dans un rapport volumique de l'ordre de 30/70.

20. Procédé selon la revendication 19, dans lequel l'étape a) comprend :

- une première opération de lavage de la phase solvant obtenue à l'issue de la co-extraction de l'uranium et du plutonium, par mise en contact de ladite phase solvant avec une phase aqueuse nitrique contenant de l'ordre de 1 à 3 moles/L d'HNO₃ ;
- une deuxième opération de lavage de la phase solvant, par mise en contact de ladite phase solvant avec une phase aqueuse nitrique contenant de l'ordre de 3 à 5 moles/L d'HNO₃ ; et
- une opération complémentaire de co-extraction de l'uranium et du plutonium de la phase aqueuse obtenue à l'issue de la deuxième opération de lavage, par mise en contact de cette phase avec une phase solvant contenant du phosphate de tri-n-butyle à 30% environ (v/v) dans un dodécane.

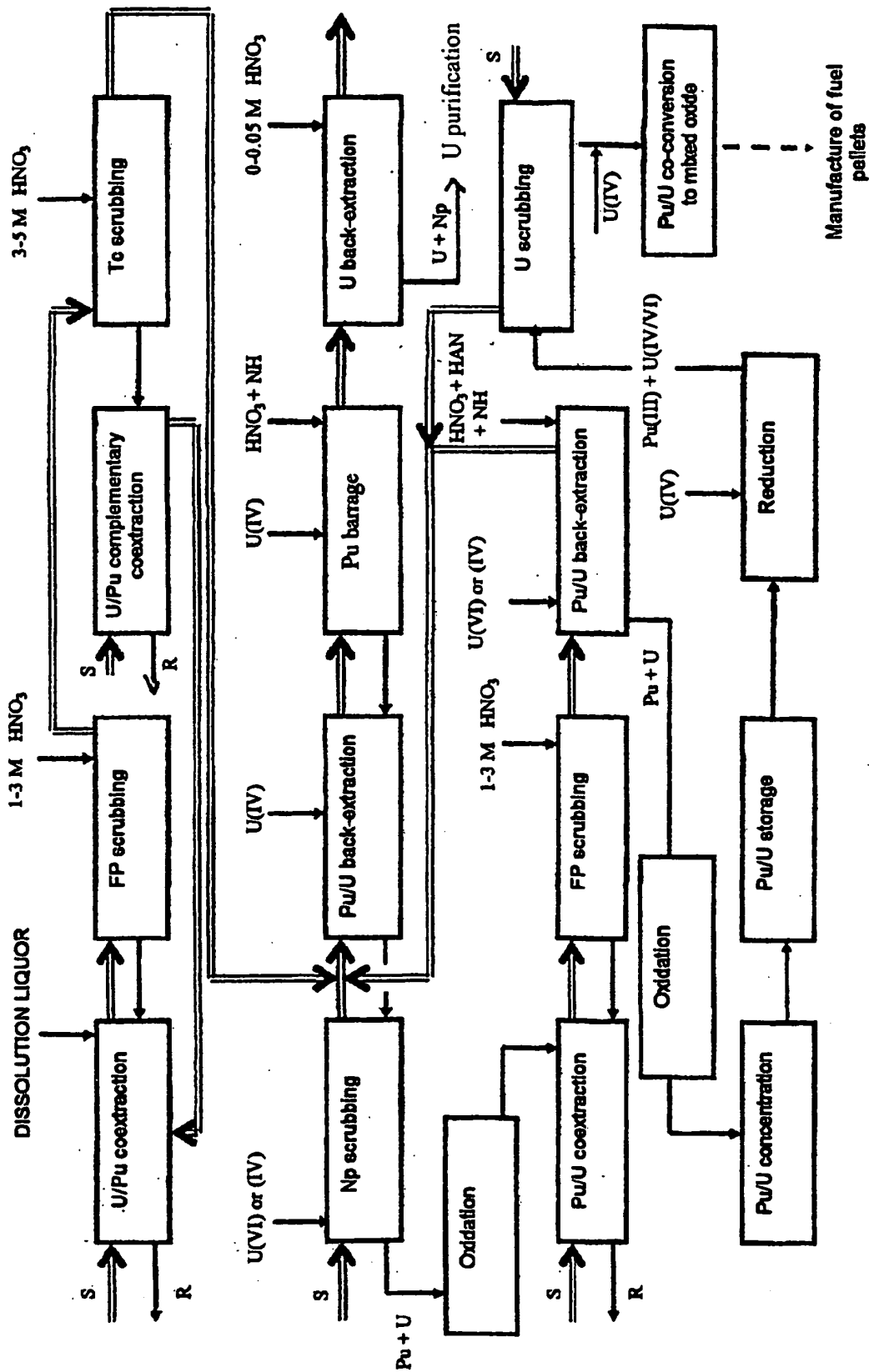


FIGURE 1

S = solvent R = raffinate
NH = hydrazine
HAN = hydroxylammonium nitrate

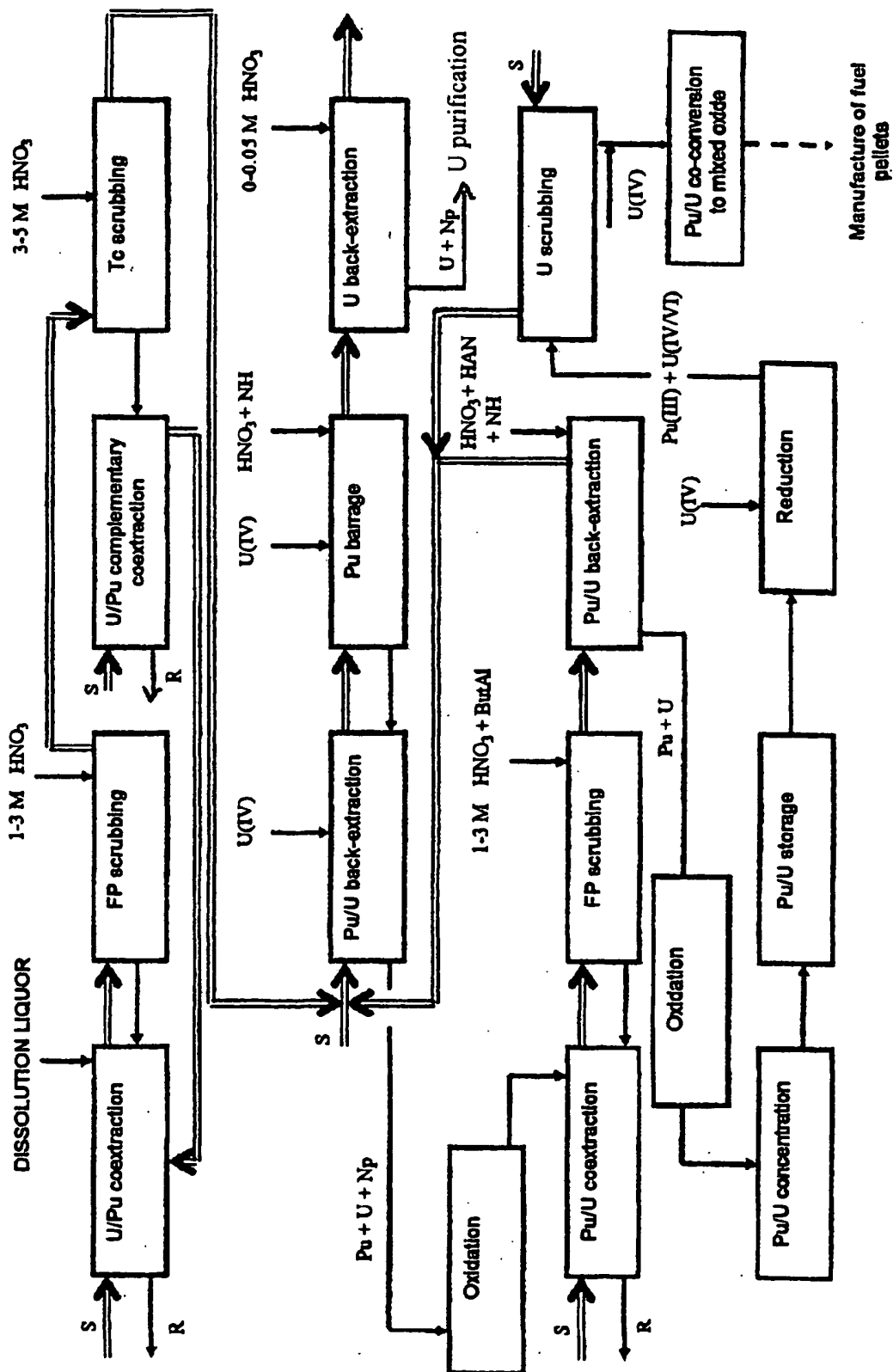


FIGURE 2

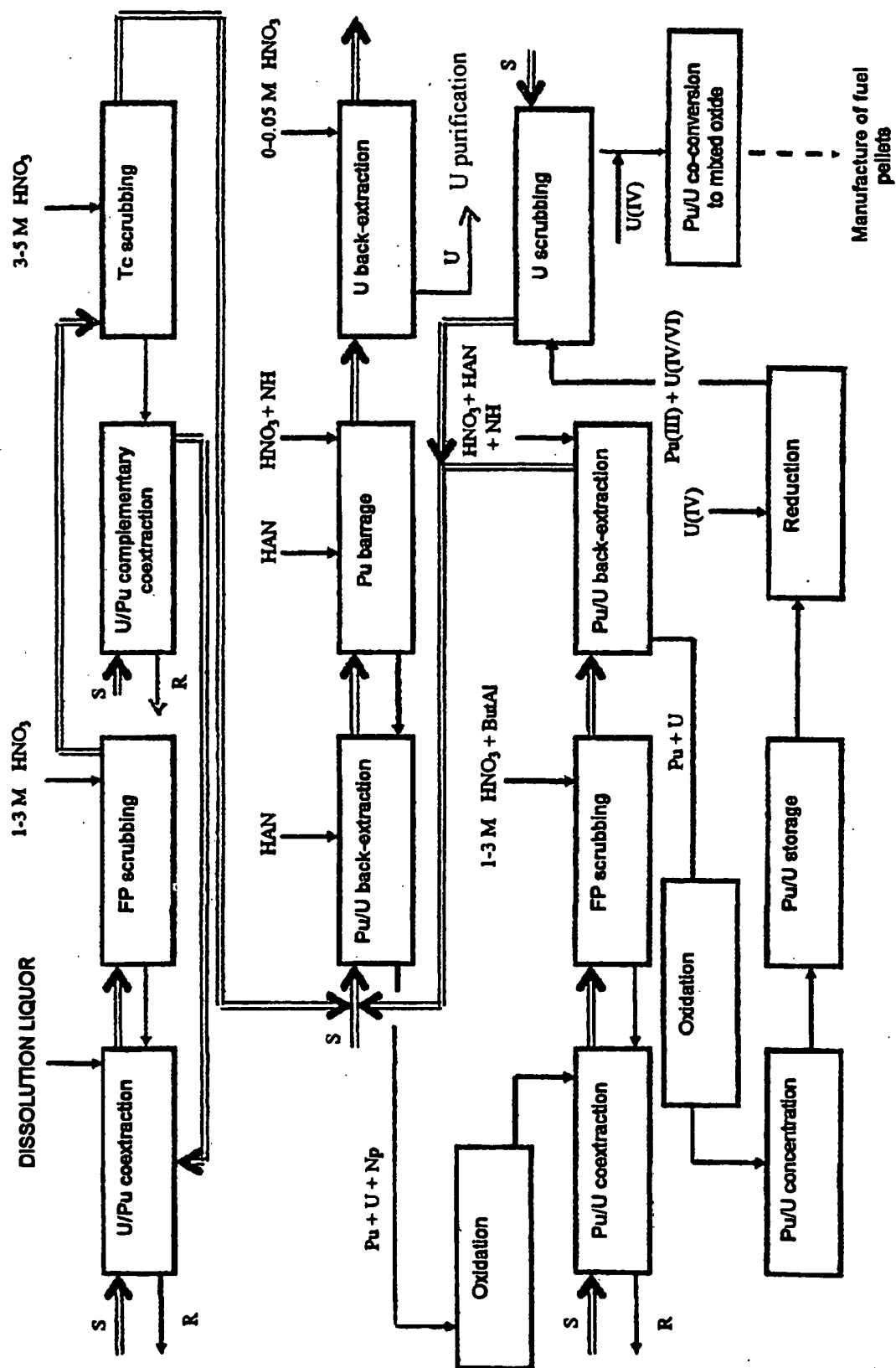


FIGURE 3

S = solvent R = raffinate
NH = hydrazine
HAN = hydroxylammonium nitrate
ButAl = butyraldehyde

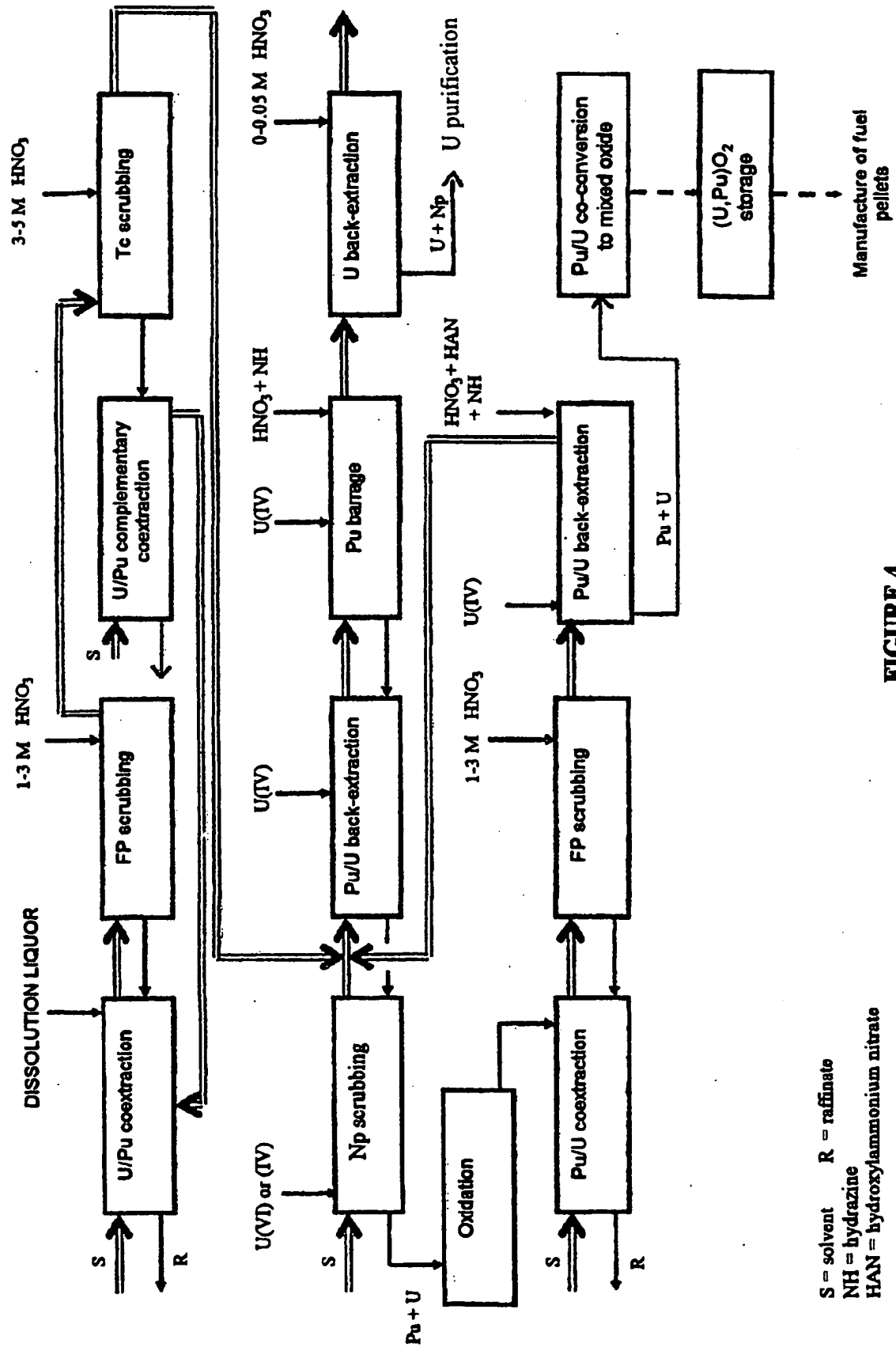


FIGURE 4

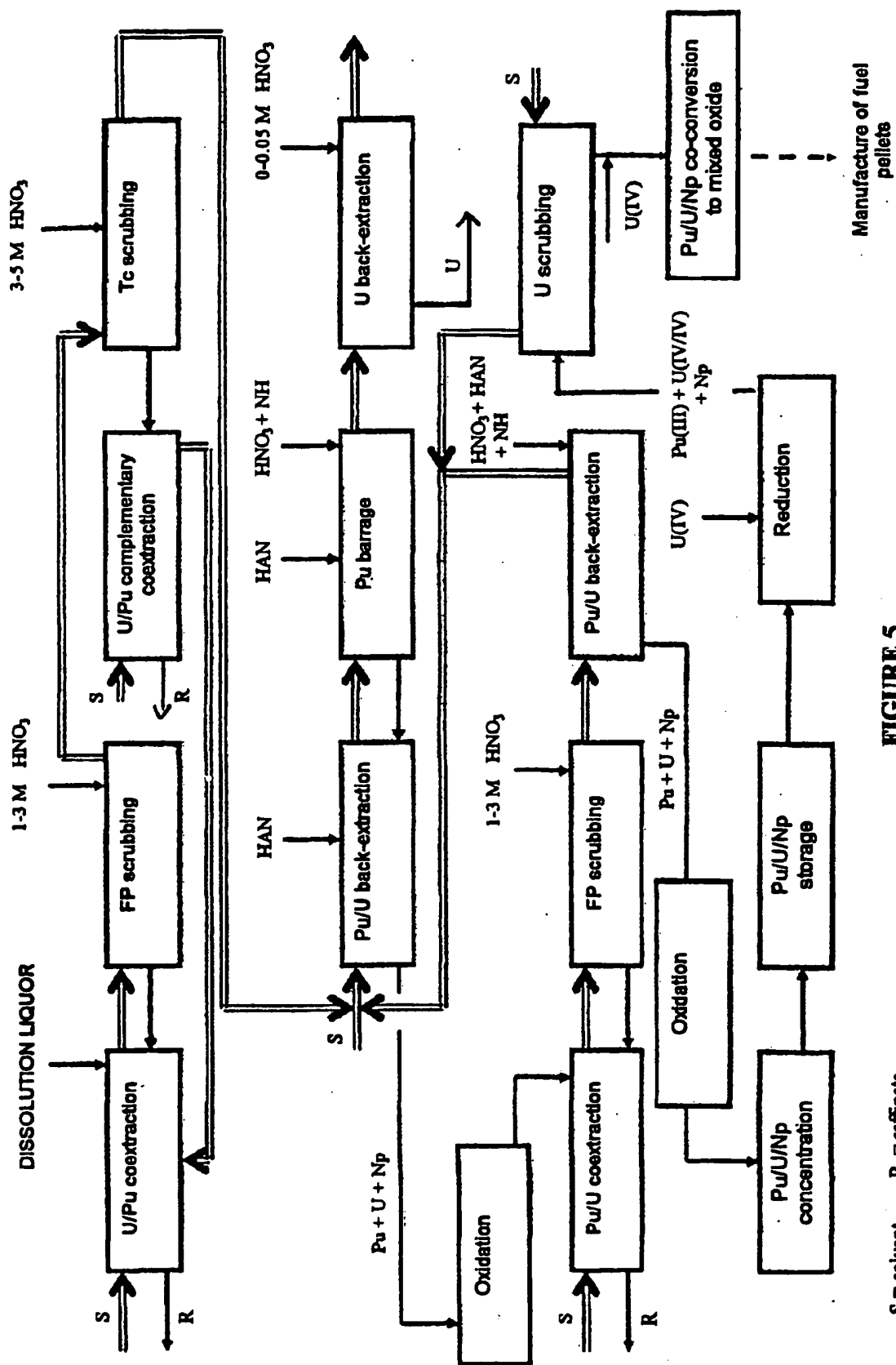


FIGURE 5

S = solvent R = raffinate
NH = hydrazine
HAN = hydroxylammonium nitrate

REFERENCES CITED IN THE DESCRIPTION

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